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Structural and Electronic Properties of RuSi, RuGe and OsSi *

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Structural and electronic properties of RuSi, RuGe and OsSi are investigated by first-principle density-functional calculations based on ultrasoft pseudopotential and generalized gradient approximations for the exchange-correlation functional. The bulk moduli for RuGe and OsSi which have not been available from experiments are predicted to be 2.08 and 2.65 Mbar. Though all these compounds with a B20 structure are semiconductors according to the calculation, their band gaps are overestimated compared to those from experiments by a factor of about two.

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In recent years, much attention has been given to semiconducting transition-metal silicides due to their practical importance in new silicon-compatible devices. However, in comparison with the well-investigated chromium and iron disilicides, there is a lack of reliable data for other compounds. More recently, the binary compounds RuSi, RuGe and OsSi have been prepared.[1−5] These compounds crystallize in the FeSi-type cubic $B20$ structure. There is a CsCl-type cubic $B2$ modification of RuSi which forms at high temperature, but no other polymorphic modifications are known of either RuGe or OsSi. Information about the electronic properties of these compounds is practically scarce and there have been only a few experimental studies up to now. Optical study[2] for RuSi showed that the high-temperature phase (CsCl-type) is a simple metal while the low-temperature phase (FeSi-type) is a semiconductor with a narrow gap of approximately 0.4 eV at room temperature. Transport and thermodynamic investigations by Hohl *et al.*[3] established that RuSi, RuGe and OsSi with the $B20$ structure are semiconductors of narrow gaps ranging between 0.15 to 0.30 eV. The structural properties had been measured for RuSi.[4] However, there are almost no data for RuGe and OsSi.

Knowledge of the electronic properties of these narrow-gap semiconducting silicides and germanides is of great importance due to their potential applications in electronics and thermoelectrics and due to possible modifications of their semiconducting properties when ternary and quaternary compounds are considered. Therefore, in this letter we present the first-principle electronic structural calculation for RuSi, RuGe and OsSi.

The calculation was based on the density-functional theory and the first-principle pseudopotential method (for details of the method see Ref. [6]). Ultrasoft Troullier–Martins-type pseudopotentials in the separable form of Kleinman and Bylander are employed for Ru, Ge, Si and Os atoms. The atomic valence configurations used to derive the pseudopotentials for Ru, Si, Ge and Os are presented in Table 1. These pseudopotentials have been tested for their bulk properties, respectively. For example, the resulting lattice constant $a_0 = 0.258$ nm (fix c/a_0=1.58), bulk modulus $B_0 = 1.90$ Mbar for Ru in the hexagonal close-packed structure agree with the experimental data. For comparison, the experimental data are $a_0 = 0.271$ nm and $B_0 = 2.20$ Mbar. For the exchange-correlation potentials we have used the Perdew–Burke–Ernzerhorf form of generalized gradient approximation (GGA). The Brillouin-zone integrations were performed on a grid of $4 \times 4 \times 4$ Monkhorst–Pack special points. The wavefunctions were expanded in a plane-wave basis with a cut-off energy of 45 Ry. A convergence test was performed with a cut-off energy up to 80 Ry. Spin-polarization is neglected in all the calculations.

Table 1. Electronic configurations used for the calculation of pseudopotentials for Ru, Si, Ge and Os.

Atom	Configuration			Cut-off radii (a.u.)			Local potential
				s	p	d	
Ru	$4d^7$	$5s^1$	$5p^0$	2.5	2.6	2.4	p
Ge	$4s^2$	$4p^2$	$4d^0$	2.1	2.0	2.5	p
Si	$3s^2$	$3p^2$	$3d^0$	1.7	1.9	2.0	d
Os	$5d^6$	$6s^2$	$6p^0$	2.5	2.7	2.5	p

Here RuSi, RuGe and OsSi belong to a family of transition-metal (TM) compounds known as the FeSi-type structure or $B20$ structure. The primitive unit cell of MB (M = Ru, Os, B = Si, Ge) contains four M and four B atoms with coordinates (u,u,u), $(0.5+u, 0.5-u, -u)$, $(-u, 0.5+u, 0.5-u)$, and $(0.5-u, -u, 0.5+u)$. To obtain the true theoretical equilibrium structure, one should relax the structure with respect to all its internal parameters. Intensive computation effort is needed for these MB compounds. Therefore, we first adopted the experimental value $u(M,B)$ for RuSi from Ref. [1], and optimized the equilibrium volume. Then we fixed the volume on the calculated equilibrium lattice constant and optimized $u(M, B)$. From a fit of the total energies to Murnaghan's equation of state, the theoretical equilibrium lattice parameters a_0 and bulk moduli B_0 were obtained. The calculated structural properties are presented in Table 2,

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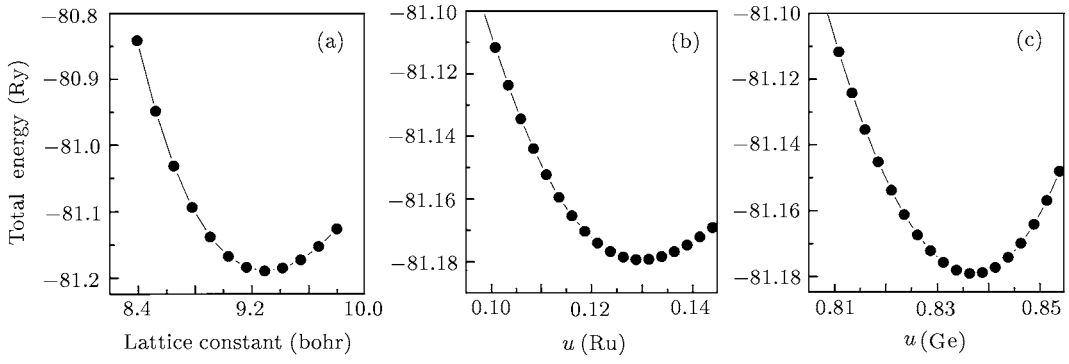

Fig. 1. Structural optimization and total energy curves obtained from our GGA calculations for RuGe.

including equilibrium lattice constants a_0, bulk moduli B_0, and the corresponding atomic coordinates $u(M, B)$. Available experimental data are given in parentheses for comparison. The internal atomic coordinates are not available from experiment for RuGe, so we present the structural optimization and total energy curves obtained from our GGA calculations in Figs. 1(a)−1(c).

From Table 2 we found that overall the equilibrium lattice parameters obtained from our GGA calculations are in good agreement with the experiments. The calculated lattice parameters differ from experiments by about 1–2%. The bulk moduli for RuSi are also in good agreement with experiments, although they were overestimated by about 14% for both the $B2$ and $B20$ structures. The bulk moduli for RuGe and OsSi are not available from experiments; we obtain 2.08 and 2.65 Mbar for these, respectively.

Table 2. Computed equilibrium lattice constants a_0, bulk moduli B_0, and the corresponding atomic coordinate $u(M, B)$ (M = Ru, Os, B = Si, Ge). Available experimental data from Refs. [1,4] are given in parentheses.

Compound	a_0 (bohr)	B_0 (Mbar)	$u(M)$	$u(B)$
RuSi ($B2$)	5.45 (5.50)	2.90 (2.55)	–	–
RuGe($B20$)	9.30 (9.16)	2.08	0.130	0.836
RuSi($B20$)	9.02 (8.90)	2.46 (2.15)	0.126(0.128)	0.834(0.836)
OsSi ($B20$)	9.13 (8.94)	2.65	0.136(0.127)	0.837(0.839)

Table 3. Eigenvalues (eV) of the top of valence (E_v) and bottom of the conduction (E_c) at the high-symmetry points of the Brillouin zone.

Compound		Γ	X	M	R
RuGe	E_v	0.00	0.19	−0.40	−0.57
	E_c	1.06	0.54	1.29	1.01
RuSi	E_v	0.00	0.20	−0.52	−0.76
	E_c	1.58	0.83	1.57	1.32
OsSi	E_v	0.00	0.00	−0.72	−1.08
	E_c	1.75	0.88	1.60	1.37

The calculated band structures for RuSi ($B2$), RuGe ($B20$), RuSi ($B20$) and OsSi ($B20$) are plotted along the symmetry lines in the simple-cubic Brillouin zone in Figs. 2(a)−2(d). The corresponding eigenvalues of the valence/conduction band maximum/minimum at the high-symmetry k point are presented in Table 3 for these compounds with the $B20$ structure.

Figure 2 clearly shows that RuSi with the $B2$ structure is a metal, and RuGe, RuSi and OsSi with the $B20$ structure are semiconductors. This is consistent with experimental results.[2] It is interesting to note that the band structures are rather similar for these compounds with the $B20$ structure. The main feature of the bands near the Fermi level involves the fact that several valence-band (conduction-band) maxima (minima) occur within a few meV of the gap edge. The calculated minimum gap is indirect and has a magnitude of about 0.34 eV for RuGe involving the valence-band maximum along the $\Gamma - X$ line and the conduction-band minimum near the X point. The gap is 0.48 eV for RuSi, and 0.74 eV for OsSi with the valence-band-maximum/conduction-band-minimum along Γ-X. Experimental measurement shows that the gaps for RuGe, RuSi and OsSi are 0.15 eV, 0.26 eV (0.40 eV^2) and 0.26 eV,[4] respectively. Comparing these indicates that the experimental gap is about half the calculated gap, i.e. the LDA overestimates the gap for this correlated electron system, in marked contrast with the case of normal semiconductor gaps and other transition-metal silicides. It is well known that the band gaps calculated within the LDA should be underestimated with respect to those from experiments for s-p bonding semiconductors, and for transition-metal silicides often quantitatively correct (for example FeSi[7]). In order to explain this, we ascribed that to the electron state near the gap. The total and projected density of states for RuSi are shown as an example in Fig. 3. From the figure we can see that the bonding properties are rather complex for these compounds. In particular, one must consider a mixture of Si–Si, Ru–Si and Ru–Ru interactions. Si–Ru 3s-4d hybridized bonds are mainly below −7.0 eV, Si–Ru 3p-4d interaction contributes in the range from −2.5 to −7.0 eV, and from 2.5 to 7.5 eV. The most dominant feature is that the states in the vicinity of the gap are essentially from Ru–Ru 4d-4d hybridization with a small proportion

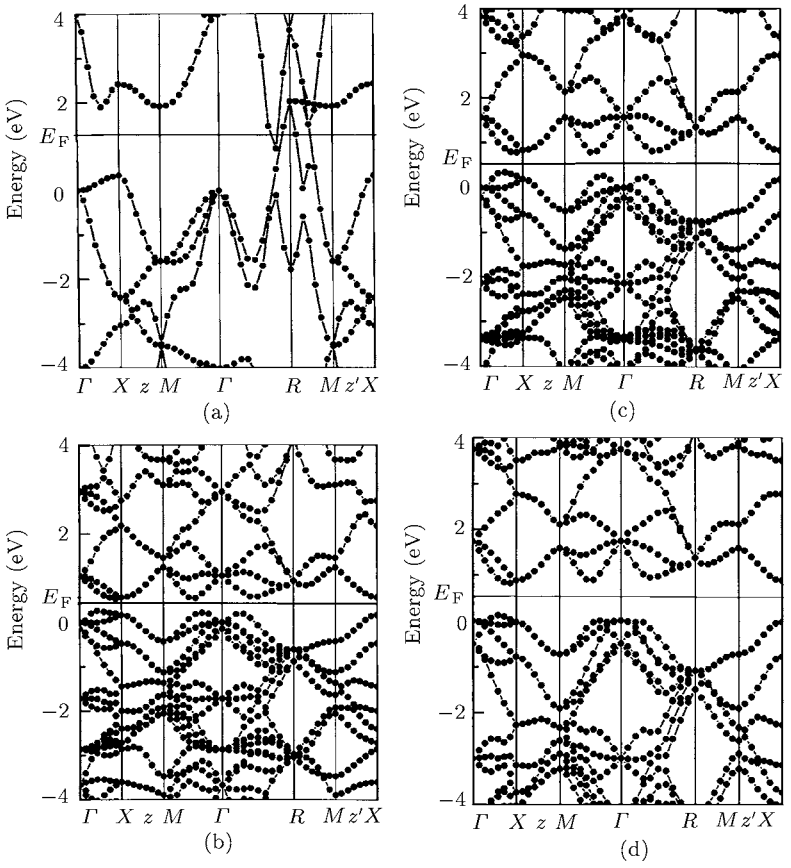

Fig. 2. Electronic band structures for (a) RuSi with $B2$ structure, and (b) RuGe, (c) RuSi, (d) OsSi with the $B20$ structure. All the energies refer to the Γ top.

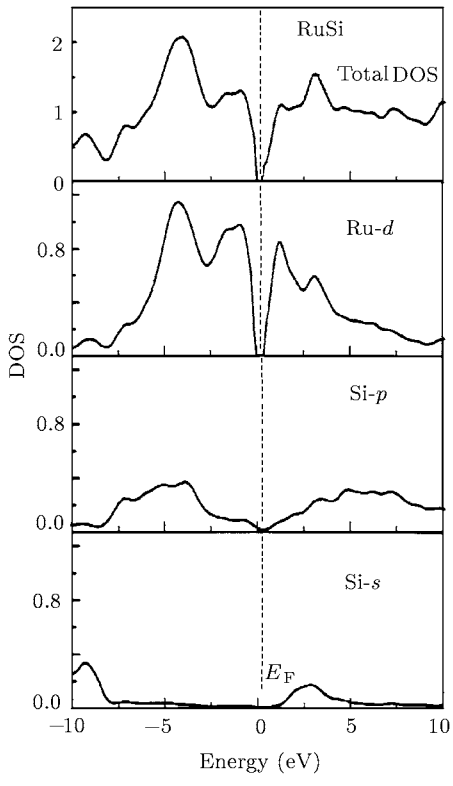

Fig. 3. Total and projected density of states for RuSi.

of Si $3s3p$ states. This is different from FeSi where the bands near the gap are hybridized by comparable Si-p and Fe-d states.[7] The d-orbital characteristics of states near the band gap may make non-local many-body corrections to the LDA results, and result in the overestimated band gaps for the compounds we studied. The mono-silicides and germanides considered here have similar configurations of the valence-electron shell and orbital compositions. The same self-consistent procedure and exchange-correlation potentials have been applied for all the compounds. Therefore, one can expect the overestimation of the energy gaps to be of the same order for all materials. However, a discrepancy exists between the experiment and our theoretical calculation. The band gaps for OsSi and RuSi are equal to 0.26 eV according to the experimental data,[4] but larger for OsSi by our calculation. In order to clarify these contradictions, researchers should perform more precise optical experiments on high-quality crystals.

In conclusion, we have studied the structural and electronic properties of RuGe, RuSi and OsSi compounds by using GGA and an ultrasoft pseudopotential approach. The calculated structural parameters are in good agreement with available experimental data for RuSi and OsSi. We have predicted the bulk moduli for RuGe and OsSi to be 2.08 and 2.65 Mbar, respectively. The internal coordinates for RuGe are determined to be u(Ru)=0.136 and u(Ge)=0.836. All these compounds with a $B20$ structure are semiconductors with indirect energy gap values of 0.34, 0.48 and 0.74 eV for RuGe, RuSi and OsSi, respectively. However, the band gaps are overestimated compared with those from experiment by a factor of two, due to the strong component of metal-d states near the gap.

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